Environmental Studies No. 32

Chemical Analysis of Samples From Experimental Northern Terrestrial Oil Spills

Northern Affairs Program

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Published under the authority of the
Hon. David E. Crombie, P.C., M.P.,
Minister of Indian Affairs and
Northern Development,
Ottawa, 1984

QS-8359-000-EF-A1
Catalogue No. R71-19/32-1985E
ISBN 0-662-13800-7

A report prepared for the Arctic Land Use Research Program of the Department of Indian and Northern Affairs.
Dr. D.M. Barnett Scientific Authority

ABSTRACT

Samples of oil-contaminated soil from Norman Wells and Tuktoyaktuk were collected and analysed some 7 and 8 years after spillage. The samples were analysed for oil content (expressed as grams of benzene extractables per gram of dry soil), by gas chromatography using a pair of packed columns (to obtain weathering information) and a capillary column (to obtain n-alkane to isoprenoid ratios which can be used as indicators of extent of biodegradation) and by liquid chromatography (to obtain a breakdown into the oil component groups of saturates, asphaltenes, polar compounds and aromatics).

The results are presented and discussed, the significant findings being that the sample analyses indicate that 30 to 50 percent of the surface oil remains (best estimate 40%) and that 40 to 68 percent of the subsurface oil remains (best estimate 52%). The oil is believed to have degraded by a combination of evaporation, dissolution and biodegradation. The proportions of each degradation process applying to each oil component group differ considerably.

Some implications regarding site monitoring and future research directions are discussed.

RÉSUMÉ

Des échantillons de sols de Norman Wells et de Tuktoyaktuk, contaminés par des hydrocarbures, ont été prélevés et analysés quelque 7 et 8 ans après les déversements. On y a dosé la teneur en hydrocarbures (exprimée en grammes de matières extractibles par le benzène par gramme de sol sec) par chromatographie en phase gazeuse en deux colonnes garnies (pour obtenir des renseignements sur la météorisation) et en une colonne capillaire (pour obtenir le rapport des n-alcanes aux isopénoides, qui peut servir d'indicateur de l'intensité de la biodégradation) et par chromotographie en phase liquide (pour connaître les taux respectifs, dans la faction huileuse, des composés saturés, des asphaltènes, des composés polaires et des aromatiques).

Les résultats sont présentés et interprétés, les conclusions finales étant que les analyses montrent que de 30 à 50 p. 100 des hydrocarbures en surface (meilleure estimation : 40 p. 100) et que de 40 à 60 p. 100 des hydrocarbures dans le sol (meilleure estimation : 52 p. 100) subsistent. On croit que les hydrocarbures se dégradent sous l'action conjuguée de l'évaporation, de la dissolution et de la biodégradation, la part de chaque processus à l'égard de chaque groupe de la fraction huileuse différant considérablement.

Certaines conséquences concernant la surveillance des placettes et l'orientation de la recherche à venir font l'objet d'une discussion.

TABLE OF CONTENTS

	Page
ABSTRACT	i
RÉSUMÉ	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	iv
LIST OF FIGURES	iv-v
INTRODUCTION	1
EXPERIMENTAL	3
2.1 Extraction	3
2.2 Gas Chromatography	3
2.3 Liquid Chromatography	5
RESULTS AND DISCUSSION	6
CONCLUSIONS	39
REFERENCES	40

LIST OF TABLES

	Page
Table 3.1 Sample locations and oil contents	10-11
Table 3.2 Capillary GC results	30
Table 3.3 Liquid chromatography results	31

LIST OF FIGURES

Figure 3.1	Norman Wells Crude Oil 12% (vol) evaporated injected directly on packed column.	14
Figure 3.2	Norman Wells Crude Oil 12% (vol) evaporated. Subjected to extraction and evaporation.	15
Figure 3.3	Sample B01 Norman Wells mature forest summer spill sample from 0 to 5 cm.	16
Figure 3.4	Sample B02 - As Figure 3.3 but from depth of 10 - 15 cm.	17
Figure 3.5	Sample B02 - As Figure 3.3 but from depth of 20 - 25 cm.	18
Figure 3.6	Sample C01 - Tuktoyaktuk Winter Spill, sample from 0 to 5 cm.	20
Figure 3.7	Sample C09 - As Figure 3.6 but from depth of 35 - 40 cm.	21
Figure 3.8	Sample C16 - Tuktoyaktuk Summer Spill Site sample from depth of 0 - 5 cm.	22
Figure 3.9	Sample C17 - As Figure 3.8, but from depth of 20 - 25 cm, showing similar n-alkane pattern.	23
Figure 3.10	As Figure 3.8 but from depth of 35 - 40 cm showing distinct n-alkane pattern.	24
Figure 3.11	Sample B08 - Norman Wells Diesel Spill.	25
Figure 3.12	Norman Wells Crude Oil subjected to extraction and evaporation.	26

Figure 3.13 Sample B04, surface oil at Norman Wells showing severe biodegradation with isoprenoid peaks dominant. 27

Figure 3.14 Sample B03 from Norman Wells at depth showing intermediate biodegradation, the isoprenoid peaks now exceeding those of the n-alkanes. 28

Figure 3.15 Speculative degradation mass balance of surface and subsurface oil. 35

INTRODUCTION

In 1972 and 1973 experimental oil spills were undertaken at Norman Wells, and Tuktoyaktuk in the Mackenzie Valley and Delta with the purpose of elucidating the physical and chemical behaviour of the oil, its biological effects on local vegetation, possible countermeasures and the likely recovery time. These spills have been described in a series of reports by Mackay et al. (1975, 1980) and by Hutchinson et al. (1975, 1978, 1981). These reports and others such as that of Johnson et al. (1980) describing the Alaskan experience contain a review of the current state of understanding of spill behaviour and effects.

With renewed interest in the construction of oil pipelines in the Mackenzie Valley, there is an additional incentive for further study, and as is addressed here, for monitoring these spill sites to determine the fate of the oil and its continued effects, some of which may be delayed. One component of such a monitoring effort is the detailed chemical analysis of the oil with a view to determining the rate of change in chemical composition. It is generally accepted that such compositional changes will influence the oil's "toxicity" to local vegetation and that these changes may occur more slowly in Northern climates because the generally lower temperatures retard evaporation and possibly biodegradation. Certainly, the oil is "trapped" in a frozen "envelope" of water for much of the year and it is unlikely that it is exposed at that time to degradative processes.

In August 1980, Dr. T.C. Hutchinson kindly collected samples of oil contaminated soil from the spill sites at Norman Wells and Tuktoyaktuk and provided them to us for chemical analysis. This report describes the

analytical methods, presents the results and discusses the findings. It is hoped that the information gained will be of value in improving scientific knowledge about spill behaviour, and will be of practical value in formulating policies for mitigating the adverse effects of spills, in taiga and tundra terrain.

2. EXPERIMENTAL

2.1 Extraction

The samples which had been taken on 5th, 12th, 13th of August, 1980 were sealed in plastic bags and stored in a freezer prior to analysis. It is unlikely that any chemical changes occurred during this time. After thawing, a weighed sample was placed in a Soxhlet thimble and extracted for at least 15 hours with benzene. Benzene is believed to be the best extracting solvent since it probably dissolves all but the highest molecular weight asphaltenic compounds. The extract was evaporated in a rotary vacuum evaporator and the mass of the residue was measured. The aim of this procedure was to separate the oil from the organic detritus and mineral matter to permit the oil content to be determined. There is a risk that during evaporation there may be loss of oil components as well as the benzene, thus the experimental approach was to err on the side of leaving some benzene in the oil. The reported oil mass fractions may thus be high. This is not regarded as a serious error since there are undoubtedly marked heterogeneities in oil contents of the soil from location to location. The values obtained should be taken as indicative of oil content at the site rather than as accurate determinations.

Table 3.1 lists the samples and their oil contents expressed as grams of extractables per gram of dry soil.

2.2 Gas Chromatography

The extracts were subjected to gas chromatographic (GC) analysis to obtain an indication of changes in volatility (i.e. loss of the lighter, more volatile components) and for measurement of n-alkane/isoprenoid ratios as an indicator

of biodegradation. This ratio changes on biodegradation as a result of normal alkanes being more easily degraded than the more "recalcitrant" isoprenoids, pristane and phytane.

Two analyses were thus done, for volatility using packed columns and for isoprenoids using a capillary column.

The packed column analysis was done with 0.5 μL samples on a Hewlet-Packard Model 700 chromatograph with a 3.0 m long by 3.0 mm o.d. column packed with 10% SE 30 ultraphase on chromosorb P, A/W, DMCS, 60/80 mesh, programmed from 50 to 280°C at 15°C per minute with a 1 minute post injection time. A flame ionization detector was used at 320°C, the injection temperature being 300°C. The output was recorded on a Shimadzu C-RIA Chromatopac integrator-recorder.

In many cases the amount of oil present was so small, or the degree of weathering was so complete, that no recognizable characteristic oil trace could be obtained. A qualitative description of the trace is given in Table 3.1 and explained in the Results and Discussion sections.

Fifteen of the better samples (indicated in Table 3.1) were further analysed using the glass capillary or open-tubular column which was 36 m long by 0.5 mm i.d. coated with OV101 in a Hewlett-Packard Model 5700A Chromatograph. This was programmed from 50 to 220°C at 4°C/minute with a 8 minute post injection time, the final temperature being held for 32 minutes. Samples of 0.9 μL were used with an injection temperature of 250°C and a flame ionization detector at 300°C. The same recorder was used as for the packed column samples.

2.3 Liquid Chromatography

Selected samples (indicated in Table 3.1) were subjected to high pressure liquid chromatographic (HPLC) analysis for determination of the contents of asphaltenes, polar compounds, aromatics and saturates. The instrument used was a Waters Model ALC - 244 Liquid Chromatograph with a μ Bondapak NH_2 column, a U6K injector, model 6000A solvent delivery system (isocratic) and a Model 440 detector absorbing at 254 n in the UV. The carrier solvent was filtered hexanes at 2.0 mL/min. The recorder was a Hewlett-Packard 3380A integrator.

A sixport Valco valve was used to backflush the column of the polar compounds.

The procedure used was to dissolve the oil in hexanes, the insoluble material being weighed and designated as asphaltenes. Aromatics were measured as they emerged from the column and polar compounds were measured after backflushing. Saturates which do not absorb in the UV were determined by difference.

3. RESULTS & DISCUSSION

Introduction:

In the interests of clarity, we first define and discuss some of the terminology of petroleum chemistry which is used in this discussion. For more comprehensive treatments the reader can consult texts such as that of Speight (1981).

Crude oil is a complex mixture of many thousands of compounds, most of which are hydrocarbons. Several groups of hydrocarbons are present of generally similar structural characteristics.

The alkanes or paraffins or saturates are the simplest group consisting of molecules such as hexane with the general formula C_nH_{2n+2} (n being the number of carbons). The molecular configuration may be linear (i.e. the normal alkanes) or branched. The normal alkanes are well characterized and appear prominently on gas chromatographic traces. The branched chain alkanes are more numerous and less well characterized. They tend to be less biodegradable. Some alkanes have cyclic or ring structures (e.g. cyclohexane) and quite complex molecules with multiple rings and branched and/or normal side chains may also be present. These are often referred to as naphthenes and are only slowly degraded microbially. Two molecules in this class are of particular interest, pristane and phytane. These are terpenoid or isoprenoid cyclic structures which are derived from plant matter and are only very slowly degraded. By measuring the ratio of a GC peak height of a normal alkane of similar volatility to that of these hydrocarbons in fresh and weathered oils it is possible to deduce if microbial degradation has occurred. The ratio tends to fall as biodegration proceeds.

The alkenes or olefins contain at least one C-C double bond and are thus "unsaturated" with hydrogen but are rarely present in crude oil.

The aromatics are based on benzene. They may have one benzene ring (monoaromatics) with normal or branched chain substituents, or they may contain several rings. These rings may be connected through side chains or they may be "fused", i.e. share common carbon atoms as in the case of naphthalene. The fused-ring compounds are termed either the polycyclic aromatic hydrocarbons (PAH) or polynuclear aromatic hydrocarbons (PNA). The aromatics are also unsaturated with respect to hydrogen and are thus the principal "unsaturates" present in the oil. Aromatics are of particular interest because they are quite soluble in water, are regarded as quite toxic, and in some cases are carcinogenic.

Large, complex aromatic molecules containing cyclo-alkane groups and side chains in various configurations are referred to as asphaltenes. They are solids which are sparingly soluble in solvents such as hexane. They are involatile and are the primary group which is left when all the other hydrocarbons have been removed.

Finally, there are hydrocarbons containing nitrogen, sulfur and oxygen in various forms (the NSO's) and metals, notably vanadium and nickel.

Only when the carbon number is less than 8 or the molecule has a particularly characteristic or common structure (e.g. pristane or a normal alkane) it is possible to identify specific hydrocarbons in an oil mixture. This problem necessitates grouping the hydrocarbons, and if quantification is desired, assignment of an average property to each group. Analyses of

weathered oil samples thus provides incomplete information about the composition of the sample, but some deductions can be made of group behaviour.

Sample Characteristics:

Table 3.1 lists the samples by number, location, depth below the surface, oil content and if packed, capillary or liquid chromotographie analyses were attemped. A quantitative statement about the quality of the packed column trace is included, "good" being a trace with a distinguishable pattern of alkanes. In many cases there was merely a poorly resolved "hump" or envelope which is probably obtained when the oil reaches an advanced state of weathering with polar and asphaltenic residues dominating.

It was noted that many of the samples retained a distinctive oily smell despite their age, indeed smell it probably a fairly good indicator of the continued presence of oil in a form in which it may exert some adverse effects, chemically or by interference with transport processes in roots.

In previous studies, we found that a very efficient and inexpensive method of detecting subsurface oil contamination was to whittle a wood stick until it was clean, then insert it into the soil to the required depth then withdraw it and smell the wood surface. It appears that this technique may be feasible for 7 to 8 years.

Amounts Present:

A considerable amount of extractable oil still remains on the sites. No accurate estimate is possible because of the small number of samples but it appears that at the Norman Wells crude oil sites there remains the following amounts expressed in g oil per g dry soil:-

0-5 cm	0.30g/g	± factor of 3
5-15 cm	0.04 g/g	± factor of 3
15 cm	.01 g/g	± factor of 3

At Tuktoyaktuk the corresponding figures are:-

0-5 cm	0.20 g/g	± factor of 3
20-25 cm	0.02 g/g	± factor of 3
30-35 cm	0.01 g/g	± factor of 4

TABLE 3.1 Sample Locations and Oil Contents.
A check mark (✓) indicates that the additional analysis was done on that sample.

Sample Number	Location & Spill Data	Depth (cm)	Oil Content g/g*	Packed Column G.C.**	Capillary Column G.C.	Liquid Chromatography‡
B01	NW Summer	0-5	0.122	good	✓	✓
B02	in Mature	10-15	0.061	good	✓	✓
B03	Forest 1972 (unburned site)	20-25	0.005	good	✓	✓
B04	NW 50 Barrel	0-5	0.592	fair	✓	✓
B05	Spill 1973	5-10	0.044	good	✓	✓
B06		20-25	0.032	poor	✓	✓
B07	NW Diesel	10-15	0.005	poor		
B08	Spill 1975	20-25	0.003	poor		
B09	NW Summer Spill	10-15	0.125	fair		
B10	in burned forest 1972	20-25	0.005	poor		
B11	NW Winter Spill	10-15	0.012	poor		
B12	1973	20-25	0.085	poor		
B13		10-15	0.027	fair		
B14		20-25	0.008	fair		
C01	Tuk Winter	0-5	0.349	fair		
C02	Spill 1974	20-25	0.025	none		
C03		35-40	0.039	fair		
C04	Tuk Winter	0-5	1.157	good	✓	✓
C05	Spill 1974	20-25	0.037	good	✓	✓
C06	(replicate)	30-35	0.011	fair	✓	
C07	Tuk Winter	0-5	0.109	good		
C08	Spill 1974	20-25	0.010	fair		
C09	(replicate)	35-40	0.010	poor		
C10	Tuk Summer	0-5	0.137	fair		
C11	Spill 1973	20-25	0.020	fair		
C12		35-40	0.000	none		
C13	Tuk Summer	0-5	0.168	fair		
C14	Spill 1973	20-25	0.006	fair		
C15	(replicate)	35-40	0.016	fair		

TABLE 3.1 Sample Locations and Oil Contents-Continued

Sample Number	Location & Spill Data	Depth (cm)	Oil Content g/g*	Packed Column G.C.**	Capillary Column G.C.	Liquid Chromatography
C16	Tuk Summer	0-5	0.316	good	✓	✓
C17	Spill 1973	20-25	0.018	good	✓	✓
C18	(replicate)	35-40	0.002	good	✓	✓
C19	Tuk Summer	0-5	0.214	poor		
C20	Spill Hill	20-25	0.049	poor		
C21	Top Site 1 1973	35-40	0.000	poor		
C22	Tuk Summer	0-5	0.070	fair		
C23	Spill Hill	20-25	0.020	none		
C24	Top 1973 (replicate)	35-40	0.000	none		
C25	Tuk Summer	0-5	0.049	fair	✓	✓
C26	Spill Hill	20-25	0.007	fair	✓	
C27	Top 1973 (replicate)	35-40	0.038	poor	✓	

* grams of extractables per gram of dry soil
** Gas chromatography

These analyses indicate that most of the oil remains close to the surface, which was, of course, the most heavily oiled layer. It is not possible from these data to deduce whether weathering is proceeding faster or more slowly near the surface.

Oil spills on arctic terrain generally cover an area of $50 m^2$ (plus or minus a factor of 3) per m^3 of oil spilled, i.e. the average depth of oil of 1/50th of a metre or 2 cm (Mackay et al. 1975, Table 6.1 and Figure 6.1). But this area may consist of a heavily contaminated region of oil approximately 10 cm deep surrounded by a much larger area of less contaminated soil. In some cases the oil may float downslope with the natural water flow. Assuming an oil density of 0.8 g/cm^3, a soil density of 1.5 g/cm^3 and a mean contamination-penetration depth of 5 cm, a mean oil content of 0.02 m^3 or 20 L or 16000 g can be expected per square metre which is equivalent to approximately 0.2 g oil/g soil, there being some 75000 g of contaminated soil to this depth per m^2. Oil contents are thus expected to vary from 0.07 to 0.6 g/g with a mean of 0.2 g/g. Shortly after the spill in heavily contaminated or oil-flooded areas there may be higher concentrations.

In most of these spill sites, the applied oil dosage was determined largely by botanical considerations, i.e. the amounts applied were judged to be in the range in which effects would be apparent, but not necessarily devastating due to massive oiling. The dosages were generally 6 to 9 L/m^2. If this quantity of oil was distributed evenly through the top 5 cm it would give concentrations of approximately 0.10 to 0.15 g/cm^3. The surface concentrations observed were often in this range and even exceeded it; thus it is apparent that much of the oil remains. If, for example, 90% of the oil had been

destroyed, it is likely that most concentrations would be in the 0.010 to 0.015 g/g range. Generally, the observed surface concentrations were in the range of 0.05 to 0.21 g/g with only 30% falling outside. In some cases (e.g. samples B04 to B06), the oil dosage was much higher since the oil was spilled at a point instead of by spraying.

It is impossible to calculate accurately from the analyses how much oil has been degraded but it is apparent that a substantial fraction of spilled oil remains. Perhaps 25 to 40% has been lost by evaporation and a further amount by other processes such as dissolution, biodegradation, oxidation and photolysis but it is likely that at least 30% remains.

It must be emphasised that this mass balance is quite speculative. In retrospect it would have been preferable to map out selected sampling sites at the time of the spill for detailed oil content analysis over the next 10 years in order that the mass of oil remaining could be determined more accurately.

Packed Column GC Analysis.

For reference purposes Fig. 3.1 is a trace obtained from the original oil and Figure 3.2 is the same oil subjected to the extraction/evaporation procedure. Although the traces differ somewhat it is apparent that most of the volatile compounds (i.e., those hydrocarbonds below C_9) are retained in the procedure.

Figures 3.3, 3.4, and 3.5 show the effect of depth on oil degradation. The near-surface oil is substantially depleted of all alkanes below C_{16}. Below

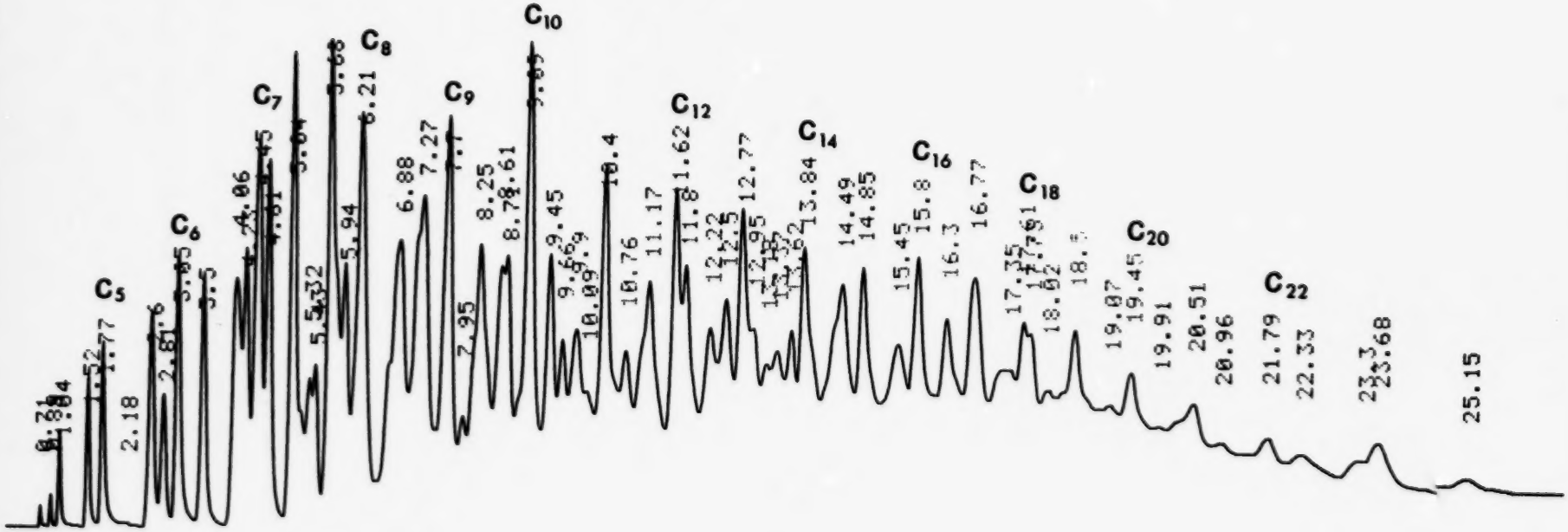


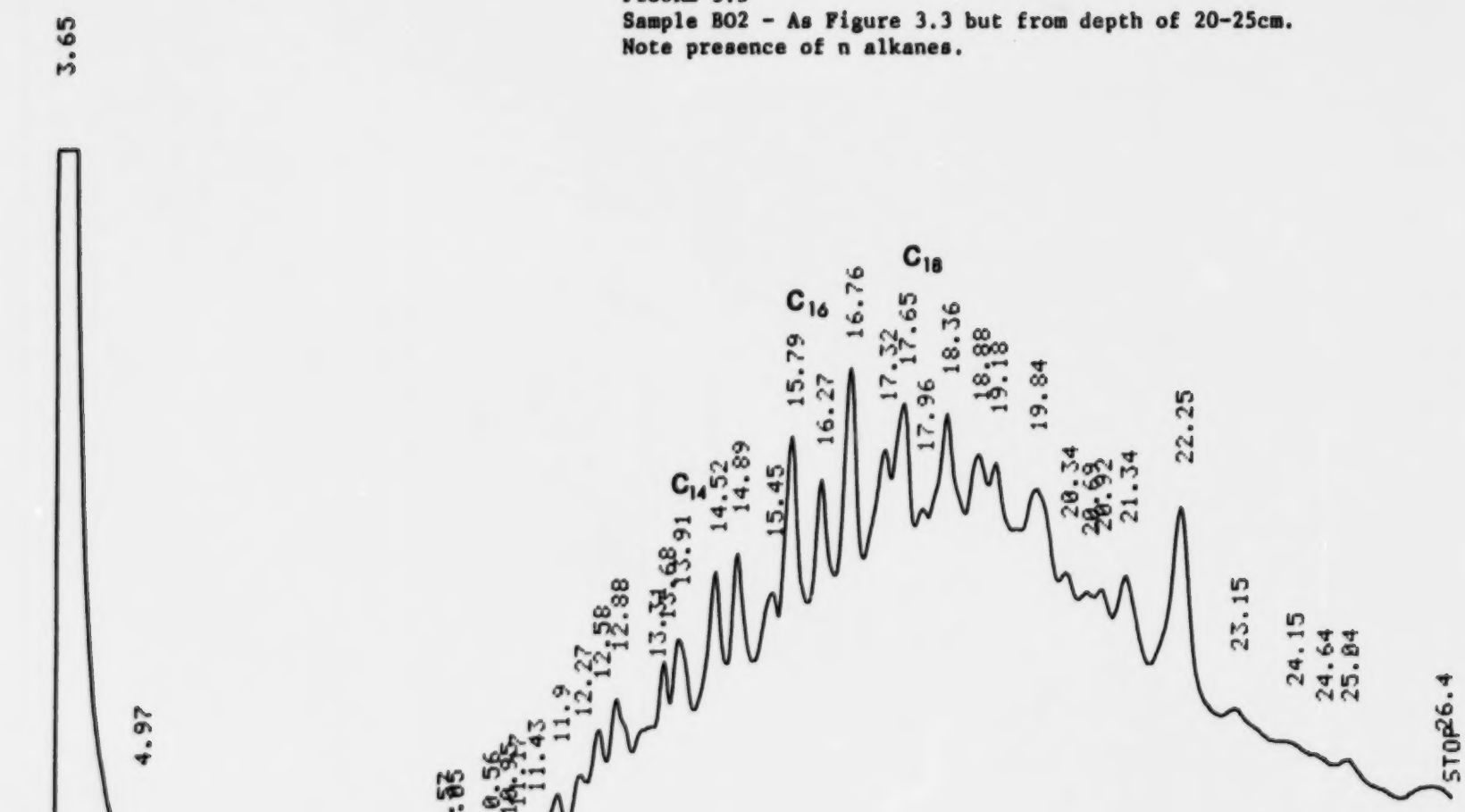
FIGURE 3.1
Norman Wells Crude Oil 12% (vol) evaporated injected directly on packed column.

FIGURE 3.2
Norman Wells Crude Oil 12% (vol) evaporated. Subjected to extraction and evaporation. Note loss of hydrocarbons below retention time of 8 minutes corresponding to C_9 when compared with Fig. 3.1.

FIGURE 3.3
Sample BOl Norman Wells mature forest summer spill sample from 0 to 5cm. Note substantial loss of n alkanes.

FIGURE 3.4
Sample B02 - As Figure 3.3 but from depth of 10-15cm.
Note presence of n alkanes.

FIGURE 3.5
Sample BO2 - As Figure 3.3 but from depth of 20-25cm.
Note presence of n alkanes.



10 cm there is some C_{14} and even a trace of C_{12} alkanes. It is clear that the surface oil has been subjected to combined evaporation and biodegradation at a greater rate than the subsurface oil.

Similar evaporative behaviour is apparent in the Tuktoyaktuk samples in Figures 3.6 to 3.10. The sample from 35-40 cm is very well preserved. It is noteworthy that the n-alkane pattern is better preserved than at Norman Wells indicating slower biodegradation. In general, the Norman Wells samples showed greater degradation than those from Tuktoyaktuk, probably because of climatic differences.

Figure 3.11 is a trace of a sample from the diesel spill site showing evidence of n-alkanes.

Capillary GC Analyses.

Figure 3.12 is a chromatograph sample of the oil subjected to the extraction/evaporation procedure.

Figure 3.13 is a surface sample from Norman Wells showing severe degradation. The pristane and phytane peaks are now dominant. The ratio of normal heptadecane (nC17) to pristane in the fresh oil is 1.17 and that for normal octadecane ($nC_1)_8$ to phytane is 1.29. The ratios in Figure 3.13 have fallen to 0.22 and 0.25 suggesting that only 18% and 19% of the alkanes remain.

Figure 3.14 shows a less degraded trace at depth in which the ratios are 0.66 and 0.74, i.e. 56% and 57% remain.

These deductions are based on the assumption that the isoprenoids degrade negligibly. This may not be a valid assumption since it is likely that even isoprenoids are slowly degraded, but at an unknown rate.

FIGURE 3.6
Sample CO1 - Tuktoyaktuk Winter Spill, sample from 0 to 5 cm. Note presence of more n alkanes than occurs in corresponding Norman Wells Sample in Fig. 3.3.

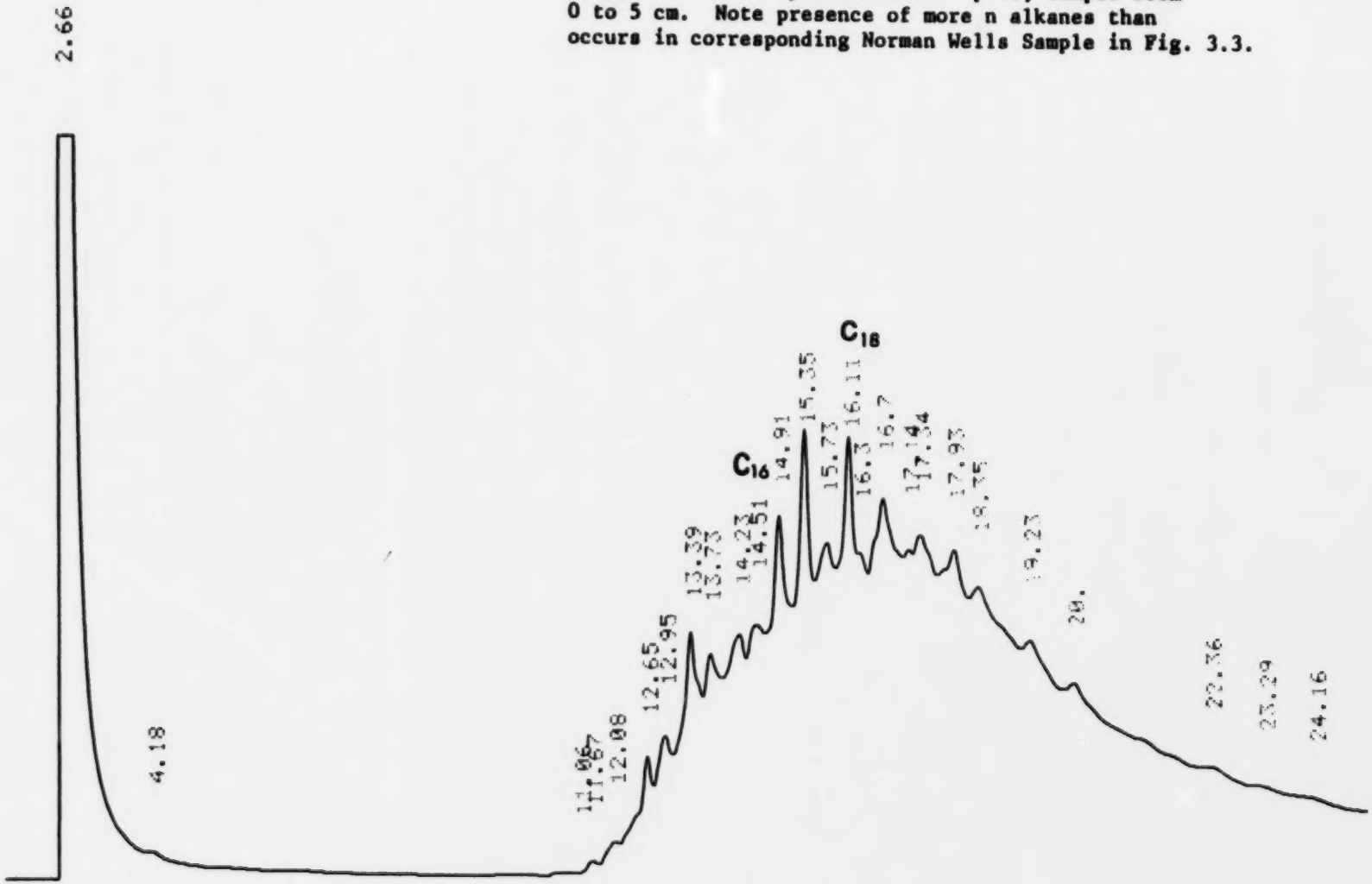


FIGURE 3.7
Sample C09 - As Figure 3.6 but from depth of 35-40cm.
Very little oil is present.

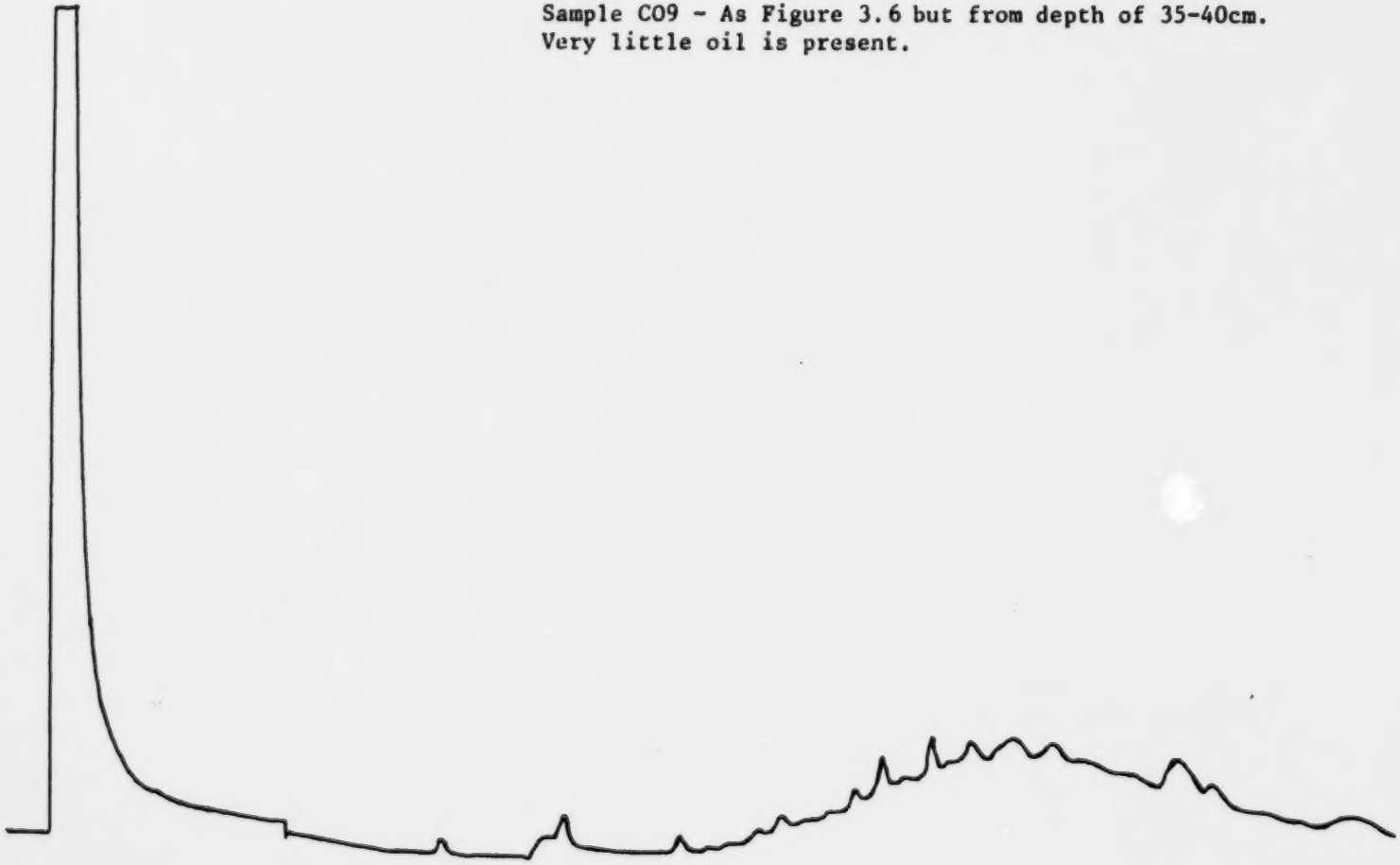


FIGURE 3.8
Sample CI6 - Tuktoyaktuk Summer Spill Site sample from depth of 0-5cm. n alkanes are still present.

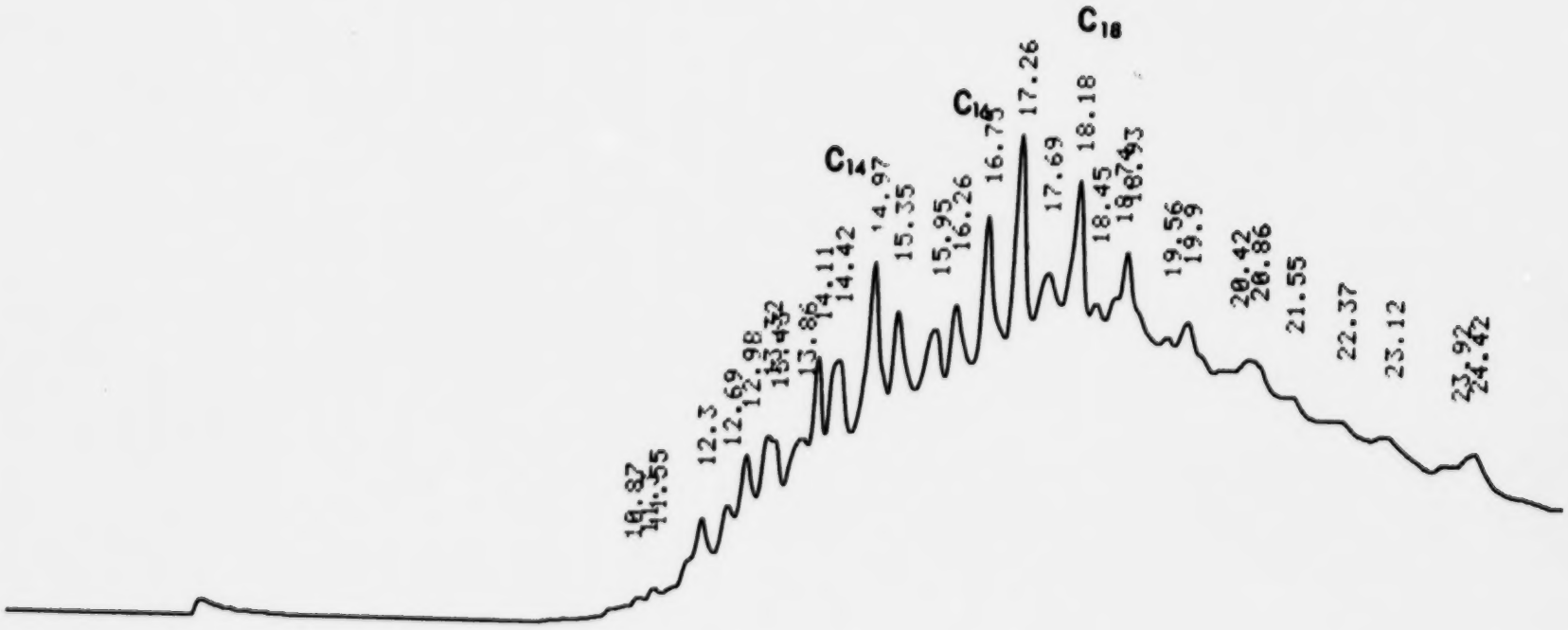


FIGURE 3.9
Sample CI7 - As Figure 3.8, but from depth of 20-25cm, showing similar n alkane pattern.

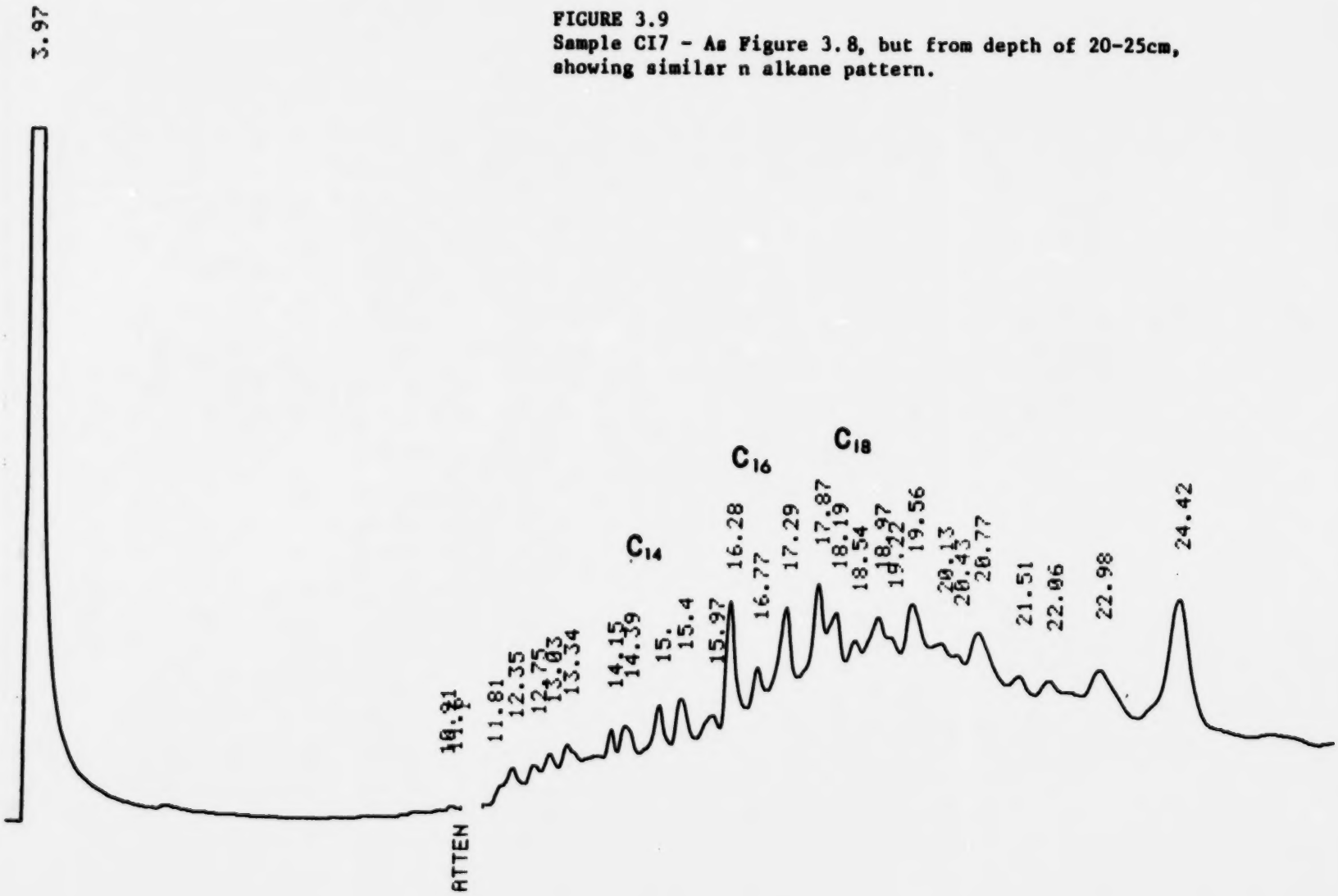


FIGURE 3.10
As Fig. 3.8 but from depth of 35-40cm showing distinct n alkane pattern.

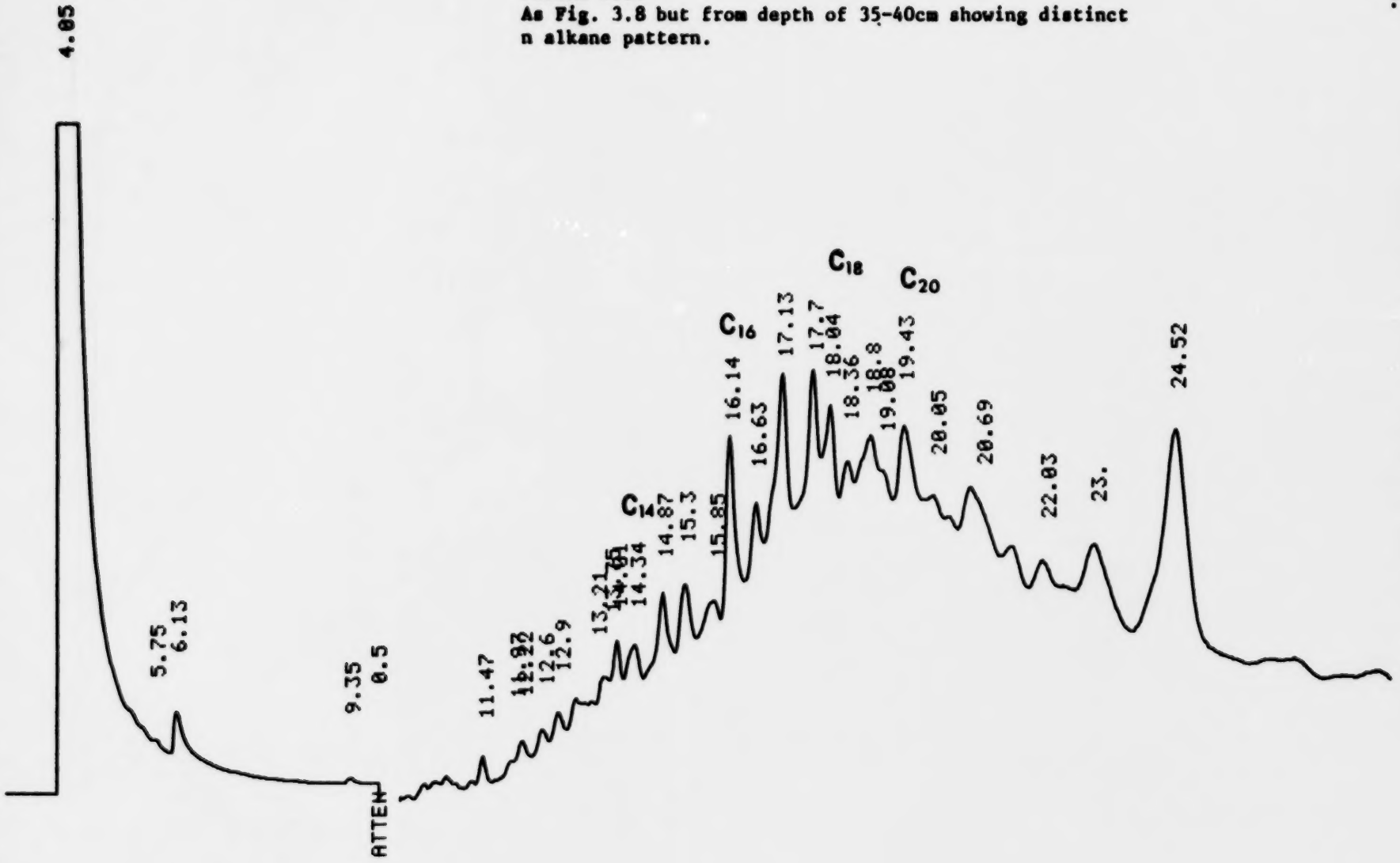


FIGURE 3.11
Sample B08 - Norman Wells Diesel Spill.

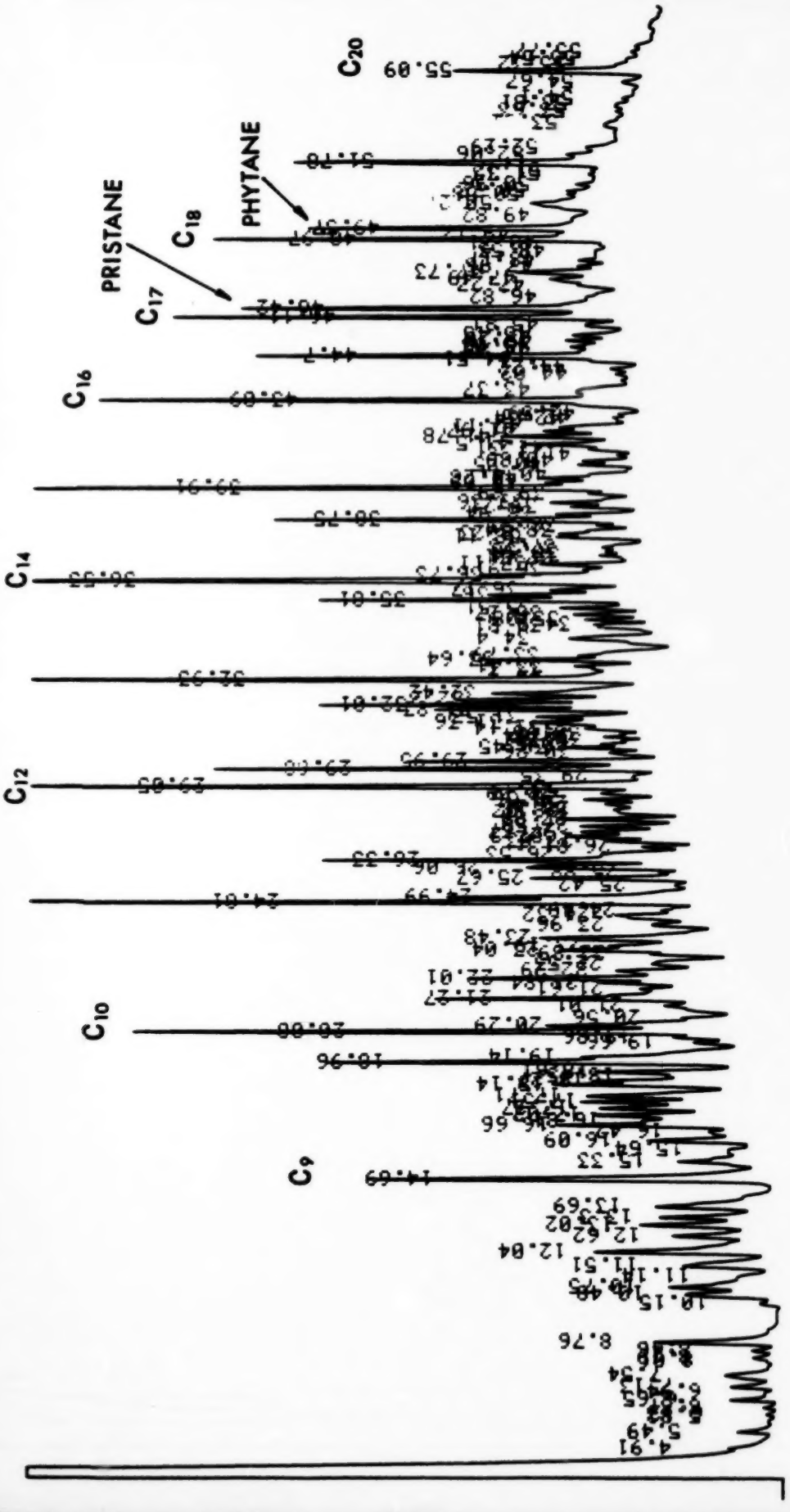
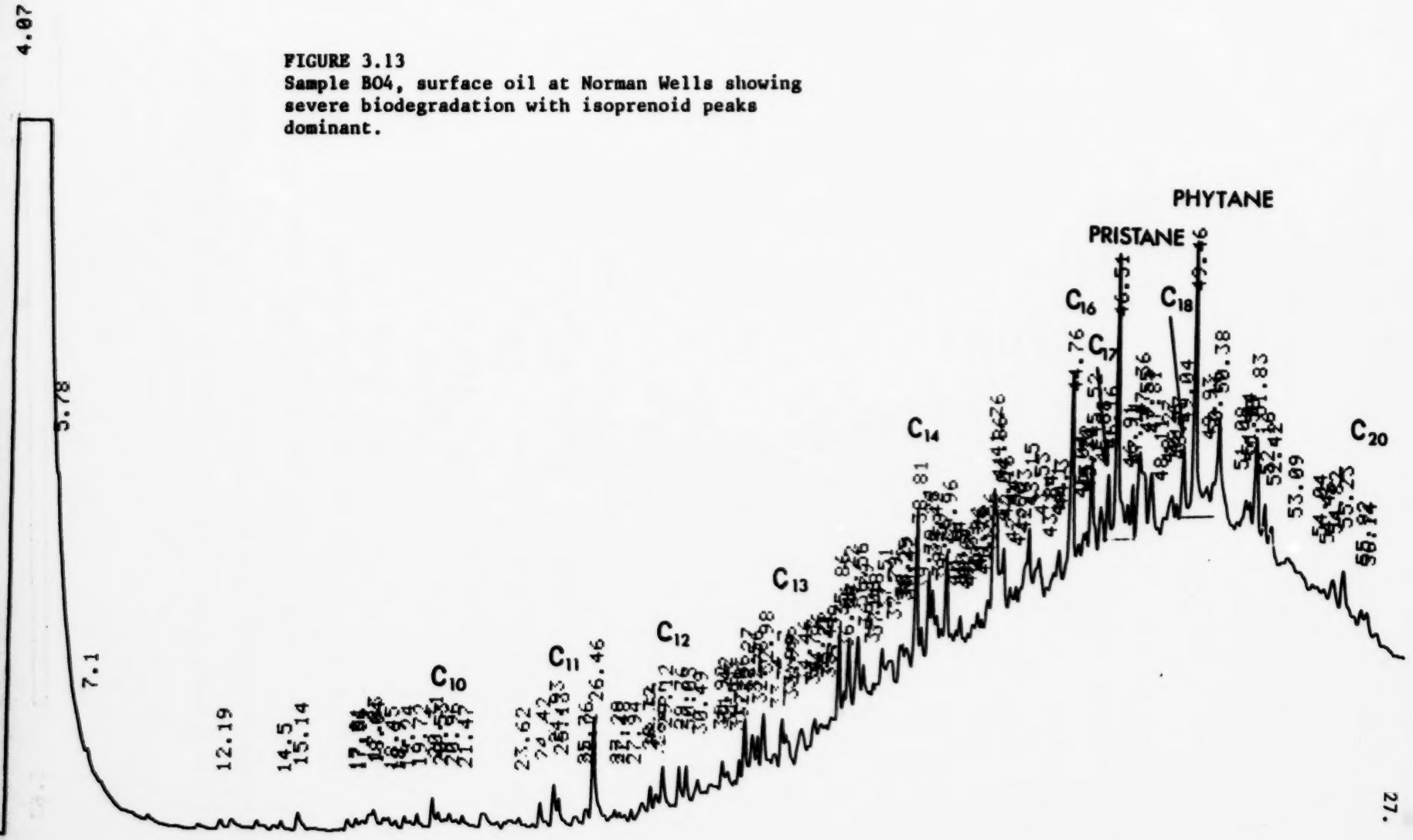


FIGURE 3.12
Norman Wells Crude Oil subjected to extraction and evaporation. Note predominance of n-alkanes over isoprenoids.

FIGURE 3.13
Sample BO4, surface oil at Norman Wells showing severe biodegradation with isoprenoid peaks dominant.



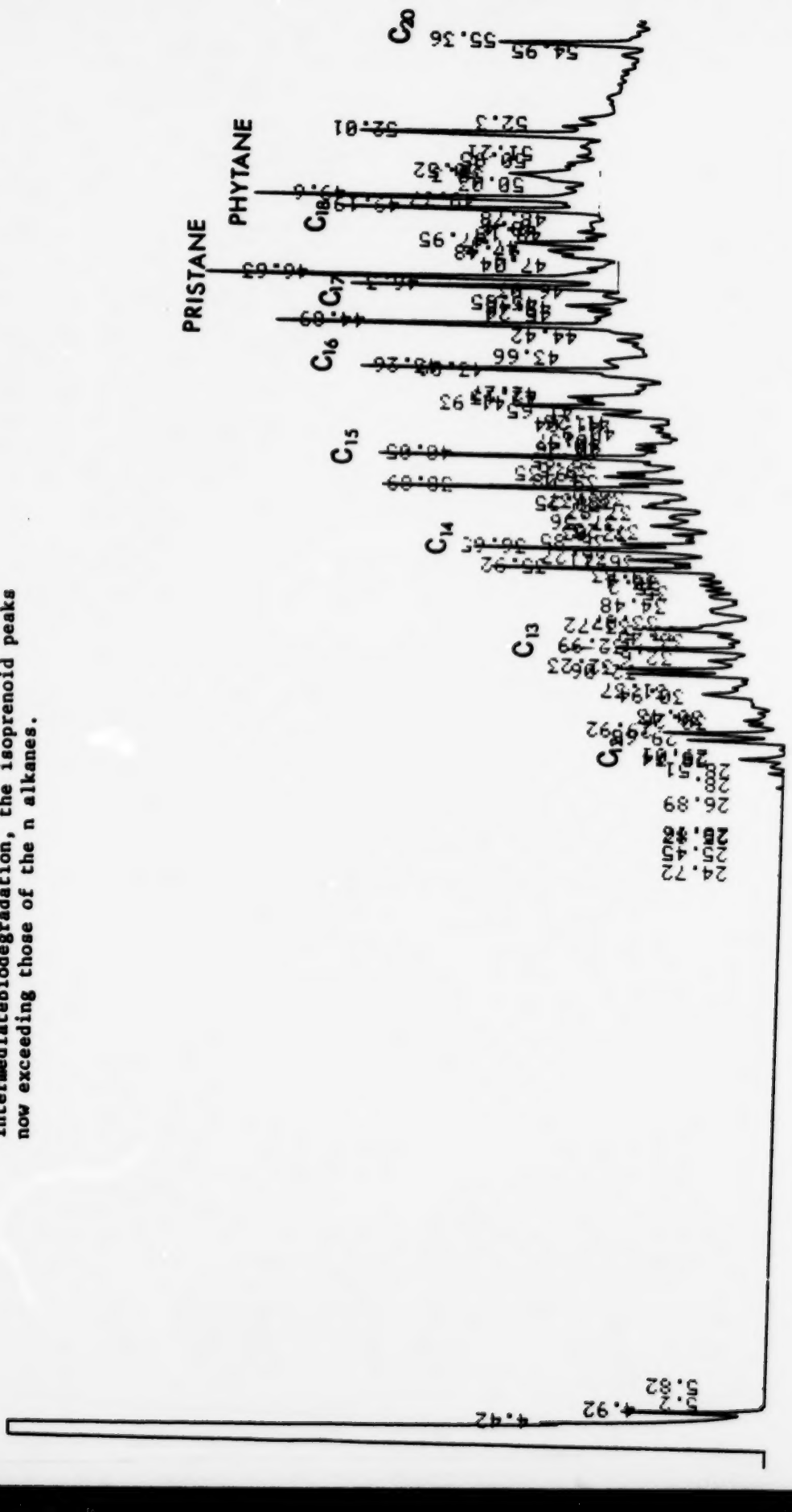


FIGURE 3.14
Sample BO3 from Norman Wells at depth showing intermediatebiodegradation, the isoprenoid peaks now exceeding those of the n alkanes.

The n-alkane/isoprenoid ratios for 12 samples are given in Table 3.2. The surface samples show the greatest degradation (greatest loss of n-alkanes) probably as a result of a longer above-freezing time and generally higher temperatures. There may also be a better nutrient supply near the surface. Biodegradation was observed in all samples with the minimum degradation being 12% in sample B05.

Liquid Chromatography:

The fresh oil analyses in Table 3.3 showed a very low asphaltene (hexane insoluble) content of 0.1%, and contents of aromatics 17.4%, polars 6.4% and saturates 76.1%. The samples from the spill sites have asphaltenes in the 0.6 to 8.3% range. It is likely that these numbers are inflated because of the extraction of hexane - insoluble ligneous materials from the soil.

The aromatic contents tend to be lower in the samples especially at depths, for example B03 and B06 show very low aromatic levels. This may be due to preferential dissolution of aromatics in ground water during the summer. Although the solubility of the aromatics is low, it is finite, and continued leaching by groundwater flow will tend to remove these compounds. For example the 2 ring aromatic naphthalene has an aqueous solubility of 30 g/m^3 thus to dissolve 1 g of naphthalene requires 0.033 m^3 or 33 L of water, assuming saturation to occur. Most 3 and 4 ring polynuclear aromatics have solubilities in the 0.01 to 1.0 g/m^3 range, thus they require larger water volumes of 1 to 100 m^3 of water per gram of oil.

TABLE 3.2 Capillary GC Results

SAMPLE	C-17 n-alkane/isoprenoid	C-18 n-alkane/isoprenoid
NW Fresh Oil	1.16	1.29
B01	0.29	0.48
B02	0.49	0.56
B03	0.66	0.74
B04	0.22	0.25
B05	1.02	1.14
B06	0.69	0.77
C04	0.08	0.10
C05	0.29	0.29
C06	-	-
C16	0.37	0.39
C17	0.62	0.67
C18	0.64	0.77
C25	0.15	0.16
C26	-	-
C27	-	-

TABLE 3.3 Liquid Chromatography Results

SAMPLE	% ASPHALTENES	% AROMATICS	% POLAR	% SATURATED
NW Weathered Oil (42% evaporated)	0.1	17.4	6.4	76.1
B01	4.1	18.4	10.1	67.4
B02	3.1	10.3	4.2	82.4
B03	6.1	5.1	2.2	86.7
B04	2.9	17.8	6.0	73.3
B05	1.8	11.6	4.8	81.8
B06	0.6	2.3	5.0	76.7
C05	2.9	5.1	2.2	89.8
C16	1.4	15.6	5.9	77.2
C17	8.3	7.3	2.8	81.6
C18	2.0	4.8	2.6	90.6
C25	3.4	15.2	4.4	77.0

The polar compounds (mainly nitrogen sulfur and oxygen species) show no distinct trends except that at depths the levels are quite low, possibly also as a result of dissolution. These compounds tend to be more water soluble than the corresponding hydrocarbons.

The saturate levels lie in the 67 to 90% range similar to that of the original oil but clearly they differ greatly in composition since the normal alkanes are depleted. It is likely that the remaining saturates are predominantly alicyclic compounds which are heavily branched and thus recalcitrant to biodegradation.

Diesel Spills:

The diesel spill chromatograms were difficult to interpret because there were no availabe data on the original oil composition and there is considerably less experience with diesel oil than with crude oil. Most effort was thus devoted to the crude oil spill samples.

Since it is likely that there will be frequent diesel spills in the North, it would be useful to develop a protocol for sample analysis and interpretation.

Summary

When interpreting the analytical data in the form of a percentage change in a given property it is essential to consider all processes as they apply to all components. Some components tend to increase in concentration when others are degraded. Thus, constancy in composition does not imply zero degradation. An attempt is made in this section to assemble an overall mass balance for the oil components for the two cases of surface and subsurface oil applicable to Norman Wells.

It must be emphasised that the deductions are somewhat speculative but the results obtained are consistent with the analyses described earlier. The original oil is taken as consisting of asphaltenes, polars, aromatics, and saturates, this latter group being broken down as normal or straight chain and branched chain, the split being an estimate made from inspection of the GC traces. The quantities are consistent with the LC analyses. The normal to branched ratio is 0.36, which is not of course equal to the n-alkane/isoprenoid ratio (here 1.17 and 1.29) because this latter ratio is only for two selected pairs of compounds. As biodegradation occurs both ratios will fall, for example if half the n-alkanes degrade, the overall ratio of normal to branched hydrocarbons will fall to 0.18 and the n-alkane/isoprenoid ratios may fall to 0.58 and 0.65.

It is assumed that evaporation occurs only to the saturates and aromatics, previous work suggesting a maximum extent of evaporation being approximately 40%. Dissolution occurs primarily to aromatics and polar compounds, the other hydrocarbons being effectively water insoluble. Biodegradation occurs to

polars, aromatics and saturates but the normal saturates are more rapidly degraded then the branched saturates by an assumed or inferred factor of six.

Figure 3.15 shows pictorially the original oil composition, its possible degradation pattern at the surface and the resulting residual oil. 60% of the oil has been removed leaving a residue which has approximately the same polar content, higher asphaltene content, a similar aromatic content, an increased branched chain alkane content and a reduced n-alkane content. The ratio of normal to branched alkanes becomes 0.07 which should correspond to a n-alkane/isoprenoid ratio of 0.23 and 0.25. These numbers are consistent with observations. The oil has now a high saturate content of 78% but most of this is branched material which is recalcitrant to biodegradation.

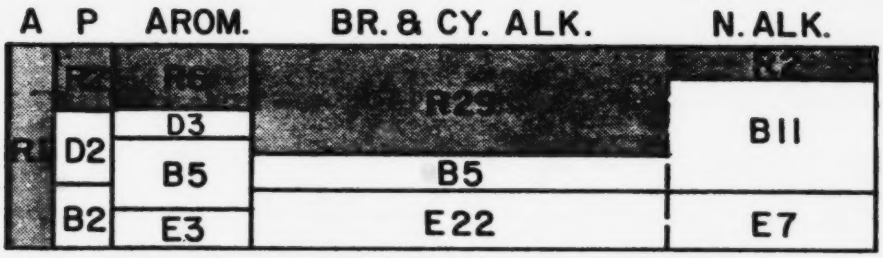
Figure 3.15 also gives a similar diagram for subsurface oil in which evaporation and biodegradation rates are reduced, and dissolution rates increased. In this case 52% of the oil remains.

Although accurate determination of the rates of each process to each component grouping is impossible, these postulations are intuitively reasonable and yield a degradation pattern which is consistent with the observed experimental data, thus it is believed that the actual situation is not far removed from that presented above.

It is unlikely that the figure of 40% remaining is less than 30% or more than 50%, i.e. error limits of a factor of 1.3 may apply.

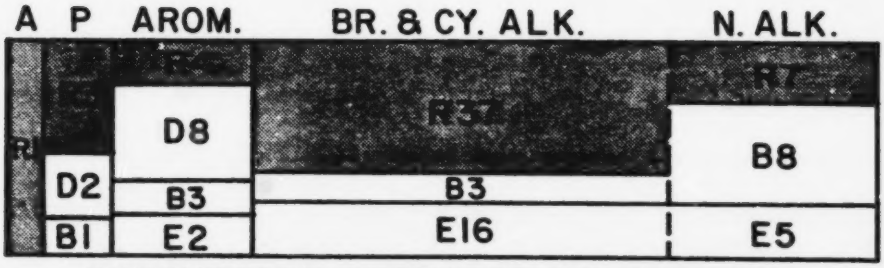
These figures apply, of course, to the oil which was trapped at the spill site. It is likely that some oil migrated out of the site in the form of colloidal particles but his process is unlikely to be continuing at an

ORIGINAL CRUDE OIL Σ = 100

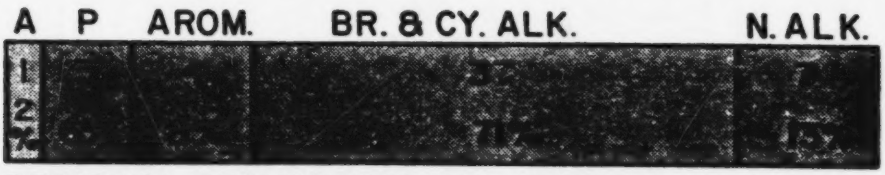


SURFACE DEGRADATION PATTERN

RESIDUAL SURFACE OIL (40% REMAINING)



SUBSURFACE DEGRADATION PATTERN



RESIDUAL SUBSURFACE OIL (52% REMAINING)

FIGURE 3.15 SPECULATIVE DEGRADATION MASS BALANCE FOR SURFACE AND SUBSURFACE OIL

KEY: R = REMAINING UNDEGRADED
D = DISSOLVED IN WATER
E = EVAPORATED
B = BIODEGRADED

appreciable rate since the oil is probably now quite firmly bound (coated) to the detrital material.

These deductions apply to Norman Wells, which is somewhat warmer than Tuktoyaktuk. In the latter location it is likely that the rates of all processess are slower, possibly by 10 to 20% but the spill conditions were quite different in the two locations and comparison is difficult. The Tuktoyaktuk GC traces showed more alkane character but the n-alkane/isoprenoid ratio reductions were similar to those at Norman Wells.

It is tempting to extrapolate into the future but any such predictions are very speculative. Evaporation will probably have little effect in the future except that possibly a few additional percent of the subsurface oil will be lost. Similarly, dissolution is likely to be slower as the less soluble compounds remain and accumulate. Perhaps another 5 to 10% may dissolve in the next ten years. Biodegradation is likely to be the dominant process but its rate is not known. It is likely that in a few years normal alkanes will be effectively eliminated, aromatics and polars will be reduced and the remaining oil will consist of high molecular weight, branched and cyclic material.

Whether or not the oil is exerting any toxic effect on vegetation presently or in the future is an issue beyond the scope of this work.

Future Directions:

This report was written in 1981, then revised in 1984. The last attempt which was made to quantify these processes was in 1979 (Mackay et al., 1980), when a simple mathematical model was compiled describing crude oil degradation processes. Since that date some progress has been made in oil spill modelling, particularly with regard to evaporation and dissolution e.g. Stiver and Mackay (1984) and Maijanen et al., (1984) and references therein. It is now possible to develop more realistic models of oil spill behaviour in soils which have the potential for greatly enhancing predictive capabilities.

The likely thrust of this work, is that for modelling purposes the oil will be broken down into a number of groups of hydrocarbons with specified ranges of properties, notably volatility, water solubility and biodegradability. The amounts in each group can be estimated by analyses and specific "marker" hydrocarbons can be identified which are present in each group. Equations can then be proposed which describe the fate of each group, i.e. the extent to which each group is subject to evaporation, dissolution and biodegradation, and the changing amounts of each group. The overall oil composition can then be calculated. It is also possible to calculate the analytically determinable quantities such as percent saturates or alkane/isoprenoid ratio which may reflect the amounts of several groups. By trial and error adjustment of the model parameters it should be possible to produce a model which is consistent with experimental observations. In addition the fate of certain specific hydrocarbons can be estimated and confirmed by analyses.

The advantage of this approach is that the analytical data will be better utilized and the need for other key data will become apparent. At present the analytical data are used only as semi-quantitative indicators of behaviour and it is very difficult to estimate fractions of oil or groups of hydrocarbons remaining. Prediction into the future is presently unreliable. It is hoped that progress in this direction can be made with a view to interpreting existing observational data more fruitfully, to designing validation experiments and ultimately to improving the capability of understanding and managing the behaviour of oil spills on northern terrain.

Finally, it is believed that the analytical protocol devised here is basically sound and could be followed in future studies. It may be preferable to do only capillary GC analyses and eliminate the packed column technique. The LC technique can probably be improved. More effort should perhaps be devoted to analyses of fuel oils such as diesel fuel which may be spilled in smaller individual amounts but more frequently during petroleum (and other) industry operations.

CONCLUSIONS

Samples of oiled soil from Norman Wells and Tuktoyaktuk have been analysed 7 and 8 years after spilling. The analyses consisted of determination of oil content, packed column and capillary column gas chromatography (the latter to obtain n-alkane/isoprenoid ratios) and liquid chromatography. The results have been presented and discussed.

The oil has undergone substantial compositional and mass changes. It is believed that at Norman Wells some 40% of the surface oil and 52% of the subsurface oil remains, these figures being subject to errors to a factor of approximately 1.3. Degradation at Tuktoyaktuk is somewhat slower.

A speculative but intuitively reasonable mass balance of the degradation processes applied to each oil component grouping has been assembled which is in accord with the experimental observations.

Some implications of these results for future work have been discussed.

It is recommended that a field manual be developed for use by environmental staff in the North giving details of likely spill behaviour and effects, remedial measures, methods of detecting and monitoring oil contamination and presenting a protocol for acquisition, storage and analysis of oil-contaminated soil samples.

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